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Sodyum Boratlardan Potasyum Borat Sentezi: Reaksiyon Koşullarının Optimizasyonu

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Anahtar Kelimeler
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Özet: Potasyum boratlar; spesifik özelliklerinden dolayı metal rafine etme endüstrisinde, yapı bileşiklerinde, fiberglas malzeme olarak, yağlayıcılarda olduğu gibi doğrusal olmayan optik malzemelerde kullanılabilen önemli bileşiklerdir. Bu çalışmada, 01-072-1688 toz difraksiyon kart numarasına sahip spesifik bir potasyum pentaborat ($KB_5O_8 \cdot 4H_2O$) olan santit minerali hidrotermal metotla %90-96 verimle sentezlenmiştir. Potasyum kaynağı olarak potasyum klorür (KCl) ve bor kaynağı olarak tinkalkonit ($Na_2B_4O_7 \cdot 5H_2O$), boraks ($Na_2B_4O_7 \cdot 10H_2O$), borik asit (H_3BO_3) ve bor oksit (B_2O_3) kullanılmıştır. Reaksiyon sıcaklıkları 60 ve 90ºC, reaksiyon süreleri 15 – 120 dakika aralığında belirlenmiştir. Sentezlenen mineraller X-Işını Kırınımı Difraktometresi (XRD), Fourier transform infrared (FT-IR) ve Raman spektroskopileri ve yüzey morfolojilerinin incelenmesi içinde taramalı elektron mikroskobu (SEM) kullanılmıştır.

Potassium Borate Synthesis From Sodium Borates: Optimization Of Reaction Conditions

Keywords
Potassium borates,
Hydrothermal synthesis,
Characterization,
XRD

Abstract: Potassium borates are the important compounds due to their specific properties and can be used as in metal refining industry, in construction compounds, as fiberglass material, as in lubricants and in non-linear optical materials. In this study, a specific potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) compound of santite mineral, with a powder diffraction number of 01-072-1688 was synthesized through a hydrothermal route with reaction efficiencies between 90-96%. The main potassium source was potassium chloride (KCl) and the boron sources were tincalconite ($Na_2B_4O_7 \cdot 5H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$), boric acid (H_3BO_3) and boron oxide (B_2O_3). Reaction temperatures were determined between 60 and 90ºC and reaction times between 15 and 120 minutes. Synthesized minerals were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and Raman spectroscopies and surface morphologies were determined by scanning electron microscopy (SEM).

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1. Introduction

Boron is found in nature as the complexes of metallic and non-metallic atoms. These complexes are called boron minerals and there are more than 230 boron minerals in nature. Each type of boron minerals is preferred in different applications according to its physical and chemical features. Potassium borates are generally used in the production of inorganic boron compounds as raw material. As a reducing agent, it is also used in photography, in metal refining and in the preparation of antibiotics and vitamins. As a potassium borate compound, potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) shows important non-linear optical features. This type of borate is also known as "santite" mineral. It has the orthorhombic lattice system and its crystals are at the appearance of transparent and colourless aggregates [1-4].

Potassium borates can be produced at dehydrated structure using the solid-state method or at hydrous structure using the liquid-state method. Youngman and Zwanziger studied the structural changes during the $(K_2O)_x \cdot (B_2O_3)_{1-x}$ formation using the raw materials of boric acid, elemental boron and potassium carbonate at the reaction temperature of 1000°C [5]. Colourless crystals of $K[B_5O_7(OH)_2]$ were synthesized using the mixture of $GaO(OH)$, H_3BO_3, KNO_3 at the reaction temperature 210°C for 3 days [6]. Wang et al., obtained $KB_3O_4(OH)_2$ from $K_2B_4O_7 \cdot 4H_2O$ phase at 165°C for 10 days [7]. $K_4[B_{10}O_{15}(OH)_4]$ was produced using the raw materials of pyridine, H_3BO_3 and KOH at 170°C for 7 days; the standard molar enthalpy of this type potassium borate was determined as 8651 kJ/mol [8, 9]. As a different kind of potassium borate, $KB_3O_5 \cdot 3H_2O$ was obtained from the reaction of $K_2B_4O_7 \cdot 4H_2O$ and $KB_5O_8 \cdot 4H_2O$ in liquid state [10]. Asensio et al., studidfed thermal behaviour of santite mineral and determined the kinetic parameters of dehydration reaction [3].

As it is seen from the literature, general synthesis procedure of potassium borate is hydrothermal synthesis and it involves the steps of raw material dissolution in liquid medium, reaction at the temperatures higher than 165°C and time longer than 3 days [5-10, 13]. The aim of this research is to optimize the reaction conditions to potassium borate synthesis at lower temperatures and times. For this purpose, synthesis parameters were selected to focus on the wide ranges of 60–90°C and 15–120 min, together with the achievement of high reaction yields from the samples. Prepared samples were identified using the technique of X-ray diffractometer (XRD) and characterized using the spectroscopic methods of Fourier transform infrared (FT-IR) and Raman. Morphological properties were investigated with scanning electron microscope (SEM).

2. Material and Method

2.1. Raw Material Preparation and Identification

The potassium source used in experiments was potassium chloride (KCl), retrieved from Sigma-Aldrich, (CAS Number P9333, with a minimum purity of 99 %) and used without any pre-treatment. Boric acid (H_3BO_3), boron oxide (B_2O_3) were determined as the boron sources and borax ($Na_2B_4O_7 \cdot 10H_2O$) and tincalconite ($Na_2B_4O_7 \cdot 5H_2O$) were used as both boron and sodium sources. The raw materials were crushed, grinded and sieve to reduce particle size below 75 µm.

The raw materials were identified by a PANalytical XPert Pro (PANalytical, Almelo, The Netherlands) X-ray diffractometer (XRD) by using Cu-K_α radiation. Operating parameters of the device were 2θ range of 7°–90°, 45 kV and 40 mA (λ= 1.53 nm).

2.2. Synthesis Procedure and Characterization of Samples

In hydrothermal synthesis, different sets were designed in potassium borate synthesis, using different boron and sodium sources. In all sets, KCl was designated as the potassium source. Each set was explained with the codes of "Kc-T-H", "Kc-T-B", "Kc-Bx-H" and "Kc-Bx-B" for Set-1, 2, 3 and 4, respectively. Each sample was encoded by letters (Kc: KCl, T: $Na_2B_4O_7 \cdot 5H_2O$, Bx: $Na_2B_4O_7 \cdot 10H_2O$, H: H_3BO_3 and B: B_2O_3), reaction temperature, and reaction time. For instance, the sample synthesized at 80°C – 15 minutes in Set-1 was coded as "Kc-T-H-80-15".

Mole ratios (mole: mole) of raw materials were determined from the pre-experiments as 1:7 for all sets. The moles of potassium and boron sources is given in Table 1. The raw materials at the suitable mole ratios were taken to the glass reaction vessel (100 ml). The reaction temperature and time were determined in the ranges of 60-90°C and 15-120 minutes.

KCl was selected as key component for the reaction yields. Calculation for the reaction yields was given in the study of Asensio et al. [3]. Expected reactions for each set were presented in (1)-(4):

$$KCl + \frac{1}{2}Na_2B_4O_9 \cdot 5H_2O + 5H_3BO_3 + xH_2O \rightarrow KB_5O_8 \cdot 4H_2O + NaCl + 2H_3BO_3 + yH_2O \quad (1)$$

$$KCl + \frac{1}{2}Na_2B_4O_9 \cdot 5H_2O + \frac{5}{2}B_2O_3 + xH_2O \rightarrow KB_5O_8 \cdot 4H_2O + NaCl + 2H_3BO_3 + yH_2O \quad (2)$$

$$KCl + \frac{1}{2}Na_2B_4O_9 \cdot 10H_2O + 5H_3BO_3 + xH_2O \rightarrow KB_5O_8 \cdot 4H_2O + NaCl + 2H_3BO_3 + yH_2O \quad (3)$$

$$KCl + \frac{1}{2}Na_2B_4O_9 \cdot 10H_2O + \frac{5}{2}B_2O_3 + xH_2O \rightarrow KB_5O_8 \cdot 4H_2O + NaCl + 2H_3BO_3 + yH_2O \quad (4)$$

Table 1. Moles of raw materials used in experiments

Sources	SET-1	SET-2	SET-3	SET-4
KCl	0.0184	0.0184	0.0184	0.0184
$Na_2B_4O_7 \cdot 5H_2O$	0.0092	0.0092	-	-
$Na_2B_4O_7 \cdot 10H_2O$	-	-	0.0092	0.0092
H_3BO_3	0.0927	-	0.0927	-
B_2O_3	-	0.0463	-	0.0463

Synthesized potassium borates were identified with XRD. The XRD parameters were remained same as defined in section 2.1. Characteristic band values of identified samples were analysed using a Perkin Elmer FT-IR with universal attenuation total reflectance (ATR) sampling accessory with a diamond/ZnSe crystal. The measurement range of 1800–650 cm^{-1}, scan number of 4, and resolution of 4 cm^{-1} were set fixed. For further analysis, Perkin Elmer Brand Raman Station 400 F was used for Raman spectroscopy. In these analyses, the exposure time was 4 seconds and the number of exposures was 4. Measurement range was 1800–250 cm^{-1} and the data interval was 2 cm^{-1}. A CamScan Apollo 300 fieldemission SEM (15kV, magnification: 2000) was used to study the surface morphology.

3. Results

3.1. Raw Material Characterization Results

The potassium source was identified as the sylvite (KCl) with powder diffraction file (pdf) number of 00-041-1476. The boron and sodium sources used in the experiments were found to be boric acid (H_3BO_3), boron oxide (B_2O_3) borax ($Na_2B_4O_7 \cdot 10H_2O$) and tincalconite ($Na_2B_4O_7 \cdot 5H_2O$) with powder diffraction file (pdf) numbers of 01-073-2158, 00-006-0297, 01-075-1078 and 00-007-0277, respectively.

3.2. XRD Results of Samples

The XRD results of synthesized potassium borates are given in Table 2. According to the XRD results, obtained samples were identified as "santite - $KB_5O_8 \cdot 4H_2O$" mineral with the pdf number of 01-1072-1688.

In all sets, the higher XRD score were obtained at the reaction temperature of 60°C. This situation may be explained with the increasing reaction temperature adversely effects the crystal structure of potassium borate hydrate. In Set-1 (Kc-T-H), XRD score of 23 was obtained at the product of Kc-T-H-90-120. The highest XRD score was 81 and it was obtained at the reaction temperature of 60°C for 15 minutes (Kc-T-H-60-15). As it can be seen from Table 2, reaction time was as important as reaction temperature. In the XRD scores of the samples synthesized in Set 2 (Kc-T-B), the reaction time had more effect than the temperature. The optimum sample of this set was Kc-T-B-60-15 and its XRD score was 70.

In Set-3 (Kc-Bx-H), the reaction temperature had more effect than the reaction time. The optimum sample was obtained at Kc-Bx-H-60-30 with the XRD score 65. In Set-4 (Kc-Bx-B), reaction time had minor effects on potassium borate formation. The optimum sample of this set was Kc-Bx-B-60-120 with the XRD score of 56. According XRD results from Table 2, Set-1 was more suitable for the santite - $KB_5O_8 \cdot 4H_2O$ formation.

XRD patterns of optimum products are presented in Figure 1. The characteristic peaks [h k l ($d_{spacing}$)] of santite can be seen at the 2θ positions of 14.92° [1 1 1 (5.93Å)], 15.85° [0 2 0 (5.59 Å)], 25.32° [0 2 2 (3.51 Å)], 26.59° [1 2 2 (3.35 Å)], 32.35° [4 0 0 (2.77 Å)] and 41.52° [4 2 2 (2.17 Å)]. The results correlate with the study of Asensio et al. [3].

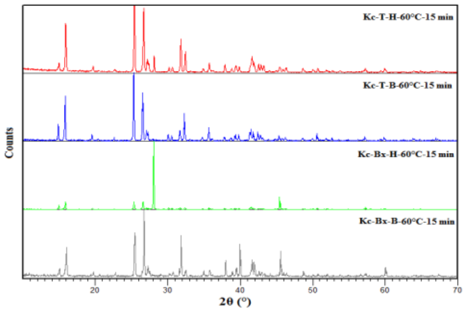

Figure 1. XRD patterns of optimum samples in each set

3.3. FT-IR and Raman Results of Samples

The boron atom is possessed of two types of coordination modes of triangularly coordinated boron atoms ($B_{(3)}$-O) and tetrahedrally coordinated boron atoms ($B_{(4)}$-O). FT-IR spectrum of optimum samples in each set is presented in Figure 2. According to the FT-IR results, the first characteristic band value in the range of 1331 - 1335 cm^{-1} could be explained with the asymmetric stretching of $B_{(4)}$-O. Bending mode of B-O-H was seen at the band value of 1245 cm^{-1}. The characteristic band between 1095-1022 cm^{-1} belonged to asymmetric stretching of $B_{(4)}$-O. Symmetric stretching of $B_{(3)}$-O was observed at around 915 cm^{-1} whereas symmetric stretching of $B_{(3)}$-O was seen at 781 cm^{-1}. Last characteristic vibrations at 690 cm^{-1} can be explained with the bending of $B_{(3)}$-O.

Table 2. XRD scores of samples

Reaction Temperature (°C)	Reaction Time (min)	SET-1 (Kc-T-H)	SET-2 (Kc-T-B)	SET-3 (Kc-Bx-H)	SET-4 (Kc-Bx-B)
60	15	81	70	65	56
	30	71	52	64	47
	60	56	55	47	51
	120	78	56	59	53
70	15	50	42	35	38
	30	42	31	35	44
	60	44	32	29	41
	120	51	31	26	23
80	15	59	46	40	37
	30	41	32	32	31
	60	45	45	33	36
	120	59	32	45	30
90	15	45	31	24	42
	30	32	36	27	30
	60	30	43	35	32
	120	23	42	21	42

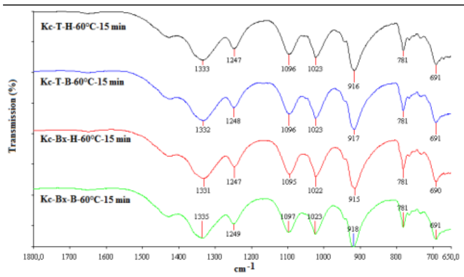

Figure 2. FT-IR spectra of optimum samples in each set

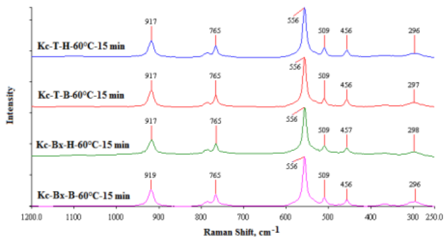

Figure 3. Raman spectra of optimum samples in each set

Raman spectrum of optimum samples in each set is presented in Figure 3. In Raman results, the band values at 917 cm^{-1} can be explained with the symmetric stretching of $B_{(3)}$-O. the symmetric stretching of $B_{(4)}$-O was observed at 765 cm^{-1}. The peak around 556 cm^{-1} was observed to the symmetric vibration of the pentaborate anion ($(B_5O_6(OH)_4)^-$). Bending of $B_{(4)}$-O was seen in the range of 509 - 296 cm^{-1}.

The obtained characteristic bands were in accordance with the results obtained by Jun et al. and Yongzhong et al [14, 15].

3.4. SEM Morphologies of Samples

SEM morphologies of optimum samples in each set are presented in Figure 4. In Set-1 and 4, potassium borate particles were seen as angular and polyhedral aggregates. Particle sizes of Kc-T-H-60-15 and Kc-Bx-B-60-15 were in the range of 292 nm – 1.80 μm and 293 nm – 1.32 μm, respectively. The unshaped particle formation were seen at the samples in Set-2 and 3. The fine particles were observed in the range of 261 nm – 1.24 μm in Set-2 (Kc-T-B-60-15), whereas the coarse particles were observed in the range of 308 nm – 2.52 µm in Set-2 (Kc-Bx-H-60-15).

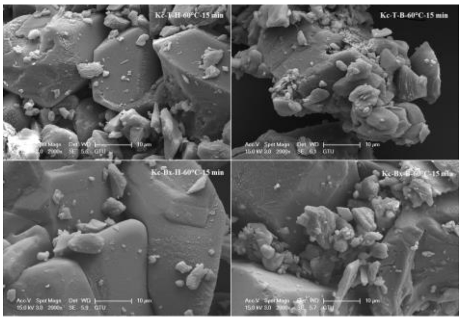

Figure 4. SEM morphologies of optimum samples in each set

3.5. Reaction Yield Results

Reaction yields results of samples are presented in Figure 5. According to the results, reaction yields increase with the increasing reaction temperature and time in all sets. The higher reaction yields were observed at the reaction temperature of 90°C and reaction time of 120 minutes. There were minor differences among the samples of sets at 90°C. The highest reaction yield was observed as 96% in Set-3 (Kc-Bx-H-90-120), while the lowest reaction yield was observed as 90% in Set-2 (Kc-T-B-90-120).

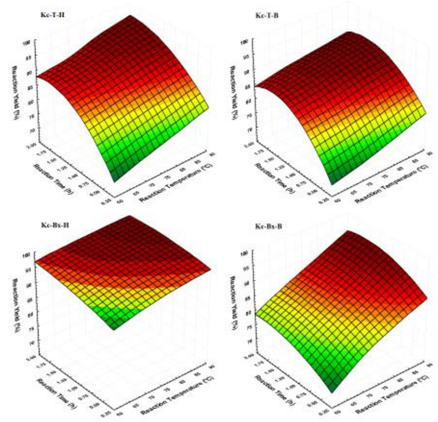

Figure 5. Reaction yields of samples

4. Discussion and Conclusion

Synthesis and characterization of potassium borates were examined in this study. Experimental results indicated the possibility of potassium borate hydrate synthesis at lower reaction temperatures and times. According to the XRD results, synthesized samples were identified as “santite - $KB_5O_8 \cdot 4H_2O$”. The highest XRD peaks were observed using the raw materials of KCl, $Na_2B_4O_7 \cdot 5H_2O$ and H_3BO_3. Characteristic vibration between the boron and oxygen atoms were determined using the FT-IR and Raman spectroscopies. In this set, angular and polyhedral aggregates were seen in the particle distribution of 292 nm – 2.52 µm.

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References

[1] Adair, A. 2007. Understanding the elements of Periodic Table: Boron, The Rosen Publishing Group, United States.

[2] Beatty, R. 2006. The Elements: Boron, Marshall Cavendish, New York.

[3] Asensio, M.O., Yildirim, M., Senberber F.T., Kipcak A.S. and Derun, E.M. 2016. Thermal dehydration kinetics and characterization of synthesized potassium borates, Research on Chemical Intermediates, vol. 42, pp. 4859-4878.

[4] Kipcak, A.S., Gunal, M., Ila, S., Yildirim, M., Piskin, M.B and Derun, E.M. 2015. Determination Optimum B_2O_3, KCl and NaOH Molar Ratios in the Synthesis of Potassium Borates, Celal Bayar

University Journal of Science, vol. 11, pp. 409-412.

[5] Youngman, R.E. and Zwanziger, J.W. 1996. Network Modification in Potassium Borate Glasses: Structural Studies with NMR and Raman Spectroscopies, The Journal of Physical Chemistry, vol. 100, pp. 16720-16728.

[6] Wu, Q. 2011. Potassium pentaborate, Acta Crystallographica, vol. E67, pp. sup-1 - sup-7.

[7] Wang. G.M., Sun, Y.Q., Zheng, S.T. and Yang, G.Y. 2006. Synthesis and Crystal Structure of a Novel Potassium Borate with an Unprecedented $[B_{12}O_{16}(OH)_8]^{4-}$ Anion, Zeitschrift für anorganische und allgemeine Chemie, vol. 632, pp. 1586-1590.

[8] Zhang, H.X., Zhang, J., Zheng, S.T. and Yang, G.Y. 2004. Two New Potassium Borates, $K_4B_{10}O_{15}(OH)_4$ with Stepped Chain and $KB_5O_7(OH)2.H_2O$ with Double Helical Chain, Crystal Growth and Design, vol. 5, pp. 157-161.

[9] Li, P. and Liu, Z.H. 2011. Standard Molar Enthalpies of Formation for the Two Alkali Metal Borates,$Na_6[B_4O_5(OH)_4]_3{\cdot}8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$, Journal of Chemical and Engineering Data, vol. 56, pp. 102-105.

[10] Salentine, C.G. 1987. Synthesis, Characterization, and Crystal Structure of a New Potassium Borate, $KB_3O_5{\cdot}3H_2O$, Inorganic Chemistry, vol. 26, pp. 128-132.

[11] Liu, Z.H., Li, P., Li, L.Q. and Jia, Q.X. 2007. Synthesis, characterization and thermochemistry of $K_2B_5O_8(OH){\cdot}2H_2O$, Thermochimica Acta, vol. 454, pp. 23–25.

[12] Alicilar, A., Okenek, F., Kayran, B. amd Tufak, M. 2015. Flame retardation, smoke suppression and antibacterial efficiencies of boron additives in styrene acrylic paints, Journal of the Faculty of Engineering and Architecture of Gazi University, vol. 30, pp. 701-709.

[13] Svanson, S. and Forslind E. 1961. Nuclear magnetic resonance study of boron coordination in potassium borate glasses, Notes, pp. 174-175.

[14] Jun, L., Shuping, X. and Shiyang, G. 1995. FT-IR and Raman spectroscopic study of hydrated borates, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 51A, pp. 519-532.

[15] Yongzhong, J., Shiyang, G., Shuping X. and Lun, L. 2000. FT-IR spectroscopy of supersaturated aqueous solutions of magnesium borate, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 56, pp. 1291–1297.